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Comparison of Rhodes's and Helsinki's Drinking Water

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The quality and features of water mainly depend on the geographical location even though significant differences can be noticed in each country's water. The most influencing causes of these differences are climate, water treatment installation technology, and last but not least, the water source. Also, it is widely known that water in the northern countries contains less minerals and salts than water in the southern countries, whose concentration of minerals and salts is higher. This contradiction is clearly caused by the climate difference as it has been observed that in southern countries, the human organism loses large proportions of salts and minerals, while in northern countries, the case is the opposite; hence, these elements have to be regained through water.

The aim of this study was to analyze and compare two different water samples from Rhodes, Greece and Helsinki, Finland by determining various parameters, and thereafter, to discover the impact of the sample's matrix on the nitrogen pollution through the determination of ammonium by using a standard addition method.

Eight basic parameters were analyzed, such as pH, hardness, conductivity, anions (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}), cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), total dissolved solids (TDS), carbonates and bicarbonates. Each measurement was repeated eight times.
For the determination of ammonium, six solutions were made for each water sample, which were considered as standard solutions. The concentrations were: 0.15 mg/l, 0.5 mg/l, 1 mg/l, 1.5 mg/l, 2 mg/l and 2.5 mg/l.

The results of the parameter determination showed that water samples from Rhodes had higher values than those of Helsinki's samples in all measurements. Some average values for Rhodes's and Helsinki's water samples, respectively, were as follows: conductivity 654 µS/cm; 154 µS/cm, hardness 287 $CaCO_3$; 54 mg/l $CaCO_3$, TDS 350 mg/l; 81 mg/l, and HCO_3 336 mg/l; 53 mg/l.
The method of standard addition and the error of the process (measurement and determination) led to a bias of 4% and a u_{bias} of 8% for Rhodes's water and to a bias of 9%, and a u_{bias} of 10% for Helsinki's water. The estimated errors for Rhodes's and Helsinki's water were 6% and 9%, respectively. There was determined statistically significant difference between Rhodes's and Helsinki's water samples' statistical analysis.

Keywords	water analysis, water quality, water parameters, matrix, ammonium

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Veden laatu ja ominaisuudet riippuvat pääasiassa maantieteellisestä sijainnista vaikka merkittäviä eroja voidaan havaita kunkin maan vedestä. Merkitsevimmät syyt, jotka johtivat näihin eroihin, ovat ilmasto, veden käsittely asennus-teknologia ja veden lähde. On yleisesti tiedossa, että vesi pohjoisissa maissa sisältää vähemmän mineraaleja ja suoloja kuin eteläisissä maissa, joissa mineraalien ja suolojen pitoisuudet vedessä ovat korkeimpia. Tämä ristiriita on selvästi aiheutettu ilmaston erosta sillä on havaittu, että Etelä-Euroopan maissa ihmisen organismi menettää isompia suola- ja mineraalimääriä kuin Pohjois-Euroopan maissa. Näin ollen, organismin pitää saada nämä elementit takaisin veden kautta.

Tämän tutkimuksen tavoitteena oli analysoida ja vertailla kahta eri vesinäytettä, Rodoksesta (Kreikka) ja Helsingistä, määrittämällä eri parametrejä ja sen jälkeen selvittää näytteen matriisin vaikutusta typen saastumiseen ammoniumin määrityksen kautta käyttämällä standardinlisäysmenetelmää.

Aluksi analysoitiin kahdeksan perusparametriä, kuten pH, kovuus, johtokyky, anionit (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}), kationit (Na^+, K^+, Ca^{2+}, Mg^{2+}), kokonaisliuenneet kiintoaineet (TDS), karbonaatit ja bikarbonaatit. Kukin mittaus toistettiin kahdeksan kertaa.
Ammoniumin määritystä varten tehtiin kuusi liuosta jokaiselle vesinäytteelle, joita pidettiin standardiliuoksina. Pitoisuudet olivat: 0.15 mg/l, 0.5 mg/l, 1 mg/l, 1.5 mg/l, 2 mg/l ja 2.5 mg/l.

Parametrien määritysten tulokset osoittivat, että kaikissa mittauksissa Rodoksen vesinäytteiden arvot olivat korkeimpia kuin Helsingin vesinäytteiden arvot. Joitakin keskiarvoja näistä mittauksista esitetään seuraavasti vastaavasti Rodoksen ja Helsingin vesinäytteistä: johtavuus 654 µS/cm; 154 µS/cm, kovuus 287 $CaCO_3$; 54 mg/l $CaCO_3$, TDS 350 mg/l; 81 mg/l ja HCO_3 336 mg/l; 53 mg/l.
Standardinlisäysmenetelmä ja prosessin (mittaus ja määritys) virhe johtivat seuraaviin tuloksiin: Rodoksen vesinäytteiden bias oli 4% ja u_{bias} oli 8%, Helsingin bias oli 9% ja u_{bias} oli 10%. Arvioidut virheet olivat vastavaasti Rodoksen veteen 6% ja Helsingin veteen 9%. Havaittiin tilastollisesti merkitseviä eroja Rodoksen ja Helsingin vesinäytteiden tilastollisessa analyysissa.

Avainsanat	Vesianalyysi, veden laatu, veden parametrit, matriisi, ammonium

Contents

1 Introduction

Water is one of the most vital sources of life in the planet. We may think that water has the same quality everywhere but it has not. Water has different features in every place of the earth, different amounts of minerals and elements. For example, in the southern countries water is harder and contains higher concentrations of minerals and dissolved salts than in the northern countries.

In this project a comparison was made between potable tap water of Helsinki, Finland and Rhodes, Greece; thus, northern and southern Europe's water. The project was carried out in the General Chemical State Laboratory of Rhodes, which is an accredited and noted laboratory in Greece. The General Chemical State Laboratory of Rhodes was built in 1929 by Italians and from that time on it has been a Chemical Laboratory. It belongs to the Greek Ministry of Finance, and uses accredited chemical methods to analyze surface water, drinking water, groundwater, bottled water, waste and treated waste water, fats, oils, alcohols and alcoholic beverages and by accredited microbiological methods to analyze drinking, surface and marine waters.

Unfortunately, due to the recent economic problems of Greece and Europe, the Chemical Laboratory of Rhodes has also been affected by the circumstances and many employees have been made redundant. Currently, in the Laboratory there are working four chemists, one of which also acts as the director/manager.

THEORETICAL PART

2 Drinking water quality standards

Drinking water quality standards set the maximum permitted concentrations of some specific water parameters. On the basis of the quality standards, it can be decided whether water is safe and suitable for consumption and use.

Many developed countries specify standards to be applied in their own country. In Europe, the European Drinking Water Directive publishes water quality standards, and in the USA, the United States Environmental Protection Agency (EPA) establishes standards as required by the Safe Drinking Water Act. For countries without a legislative or administrative framework for such standards, the World Health Organization publishes guidelines on the standards that should be achieved. [1]

2.1 EU's drinking water quality standards

Drinking water quality standards that have been applied in the European Union are valid in Finland and Greece.

Table 1, 2 and 3 present the EU's drinking water standards (Council Directive 98/83/EC adopted by the Council, on 3 November 1998). [2] The quality standards are divided in three categories: chemical parameters (Table 1), indicator parameters (Table 2), and microbiological parameters (Table 3).

Table 1. Drinking water quality standards for chemical parameters. [2]

Chemical parameters	**Symbol/formula**	**Parametric value (mg/l)**
Acrylamide	C_3H_5NO	0.0001
Antimony	Sb	0.005
Arsenic	As	0.01
Benzene	C_6H_6	0.001
Benzo(a)pyrene	$C_{20}H_{12}$	0.00001
Boron	B	1.00
Bromate	Br	0.01
Cadmium	Cd	0.005

Chromium	Cr	0.05
Copper	Cu	2.0
Cyanide	CN =	0.05
1,2-dichloroethane	Cl CH_2 CH_2 Cl	0.003
Epichlorohydrin	C_3H_5OCl	0.0001
Fluoride	F	1.5
Lead	Pb	0.01
Mercury	Hg	0.001
Nickel	Ni	0.02
Nitrate	NO_3	50
Nitrite	NO_2	0.50
Pesticides		0.0001
Pesticides - Total		0.0005
PAHs		0.0001
Selenium	Se	0.01
Tetrachloroethene and trichloro-ethene	C_2Cl_4/C_2HCl_3	0.01
Trihalomethanes - Total		0.1
Vinyl chloride	C_2H_3Cl	0.0005

Table 2. Drinking water quality standards for indicator parameters. [2]

Indicator parameters	**Symbol/ formula**	**Parametric value**
Aluminium	Al	0.2 mg/l
Ammonium	NH_4	0.50 mg/l
Chloride	Cl	250 mg/l
Clostridium perfringens (including spores)		0/100 ml
Colour		Acceptable to consumers and no abnormal change
Conductivity		2500 µS/cm @ 20 ^oC
Hydrogen ion concentration	$[H^+]$	≥ 6.5 and ≤ 9.5
Iron	Fe	0.2 mg/l
Manganese	Mn	0.05 mg/l
Odour		Acceptable to consumers and no abnormal change
Oxidisability		5.0 mg/l O_2
Sulfate	SO_4	250 mg/l
Sodium	Na	200 mg/l
Taste		Acceptable to consumers and no abnormal change
Colony count 22o		No abnormal change
Coliform bacteria		0/100 ml
Total organic carbon (TOC)		No abnormal change
Turbidity		Acceptable to consumers and no abnormal change
Tritium		100 Bq/l
Total indicative dose		0.10 mSv/year

Table 3. Drinking water quality standards for microbiological parameters. [2]

Microbiological parameters	**Parametric value**
Escherichia coli (E. coli)	0 in 100 ml
Enterococci	0 in 100 ml
Pseudomonas aeruginosa	0 in 100 ml
Colony count 22 ^{o}C	100/ml
Colony count 37 ^{o}C	20/ml

3 Drinking water treatment

Clean and safe potable water is highly important for everyday life; therefore, it has to be treated prior to consumption. Water treatment includes industrial-scale processes that make water more suitable for consumption and use. The aim of water treatment is to remove the existing water contaminants or to reduce their concentrations in order to reach the desired goal, which is a safe and pure product suitable for consumption.

Drinking water sources are prone to contamination and require appropriate treatment to remove disease-causing agents. Public drinking water systems use various methods of water treatment to provide safe drinking water for their communities. [3]

Water may be treated differently in different communities and in different countries depending on the quality and type of water, which enters the plant. Groundwater normally requires less treatment than surface water due to the fact that surface water contains more sediment and pollutants and is more likely to be contaminated than groundwater, which in most of the cases gets naturally filtrated by percolating through the soil. [3;4]

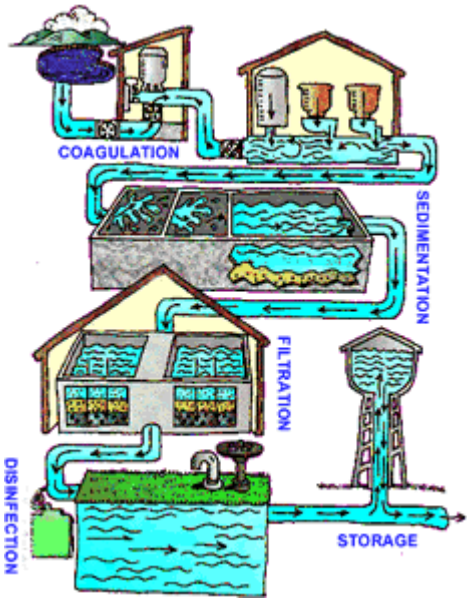


Figure 1. Drinking water treatment processes. (Courtesy of EPA) [4]

Figure 1 above shows the most common steps in water treatment, mainly in surface water treatment, used by community water systems. These processes include coagulation and flocculation, which are often the first steps in water treatment [4]. During this stage of the treatment process, chemicals with a positive charge are added to the water. The positive charge of these chemicals neutralizes the negative charge of dirt and other dissolved particles in the water. When this occurs, the particles bind with the chemicals and form larger particles, called floc.

The next step of the treatment process, the floc settles to the bottom of the water supply, due to its weight. [4] This settling process is called sedimentation.

Once the floc has settled to the bottom of the water supply, the clear water on top will pass through filters of varying compositions (sand, gravel, and charcoal) and pore sizes, in order to remove dissolved particles, such as dust, parasites, bacteria, viruses, and chemicals. [4] This process is called filtration.

After the water has been filtered, a disinfectant (for example, chlorine or chloramine) may be added in order to kill any remaining parasites, bacteria, and viruses, and to protect the water from germs when it is piped to homes and businesses [4]. This remarkably important process is called disinfection.

Once treated, the water is transmitted to treated water storage, which could be above or below ground. The final component of the system is the distribution method to individual homes, businesses and public use. [4]

3.1 Drinking water treatment in Rhodes

Water prior to treatment is raw. It contains various solids such as dirt and mud as well as germs and microorganisms that are not visible to the naked eye. After being treated (screening, flocculation, sedimentation, filtration, disinfection) water is free of the above-mentioned impurities. [5]

In Greece and also in Rhodes the water treatment sequence that is reported below is followed for treating raw water.

Chlorine is added to the water. By prechlorinating the water, microbes that are present in it are being killed, which facilitates the subsequent process. [5]

Then, aluminum sulfate is added. The solution of aluminum sulfate helps the solid particles present in water to aggregate together and after gaining a larger weight to settle. [5] The whole process is called flocculation.

After flocculation the agglomerated solids (flocs) are precipitated at the bottom of the settling tank. In this way the water is purified at 80%. [5] This process is called precipitation.

Then, during filtration, the very light particles that have not been precipitated are being retained in special sand filters from which the water comes out cleaner and may be offered to consumption. [5]

If Prechlorination is not satisfactory, additional chlorine can be added while water is entering the closed storage tanks and before entering the water supply. [5]

3.2 Drinking water treatment in Helsinki

The raw water from Lake Päijänne is treated at the water treatment plants in Pitkäkoski and Vanhakaupunki in order to obtain clean domestic water. The water treatment processes of the two water treatment plants are the same. [6]

Raw water is precipitated with ferrous sulfate, and then is stirred and mixed in order to remove possible existing humus and to improve purity. After that, the precipitate is separated from the water in settling tanks and sand filters. [6]

Microbes that may exist in the water are killed by ozone, which also improves the odor and taste of the water. Then, carbon dioxide is added, which increases the alkalinity of the water; thus, the corrosion of water pipes is being reduced. [6]

The remaining organic matter is removed by activated carbon filtration, after which water is disinfected by UV light. Finally, chlorine or chloramine is added to the water in order to reduce microbial growth in the distribution network. The pH of the water is adjusted with lime water, and the alkalinity is regulated with carbon dioxide. [6]

The whole treatment process of Helsinki's water is demonstrated in Figure 2.

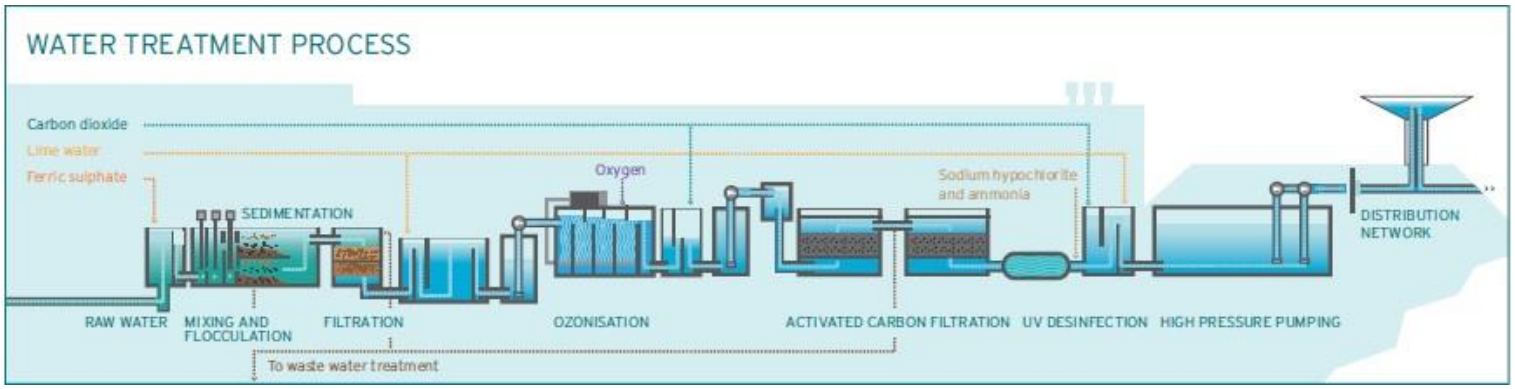


Figure 2. Drinking water treatment process in Helsinki. [6]

4 Hydrologic cycle

Hydrologic cycle is the constant movement of water above, on, and below the earth's surface. [7, p.190]

Water in its three phases (gas, liquid, and solid), starting from the ocean, land, or living matter moves into the atmosphere by evaporation and transpiration. It passes through complicated atmospheric phenomena, generalized as the precipitation process, back to earth's surface, upon and within which it moves in a variety of ways and is incorporated into nearly all compounds and organisms. [8, p.39-40]

It can be concluded that the oceans are the immense reservoirs from which all water originates and to which all water returns. This simple statement may be further explained as follows: water evaporates from the ocean, forms clouds which move inland, condenses, and falls to the earth as precipitation. From the earth, through rivers and underground, water runs off into the ocean. These processes are presented in Figure 3. So far, there is no evidence that water decreases in quantity at a global level. No water is depleted, but none is generated either, and that is according to the law of conservation of matter. For human usage, however, the physical state of water is important and so its quality, since increases in human population and levels of industrialization have produced growing demands for more water of better quality. Unfortunately, anthropogenic activities also impact water quantity and quality and therefore define human access to potable water. This results in the limited availability of water while the need for it, is ever increasing, and consumption is bound to exceed the ceiling of supply. In recognition of this basic human need for water, in the past few years industrialized nations have developed programs to restore the quality and the quantity of their natural freshwater and saltwater resources. Therefore, water conservation and pollution abatement have become very important in today's economic life. [8, p.39-40; 24, p.4153]

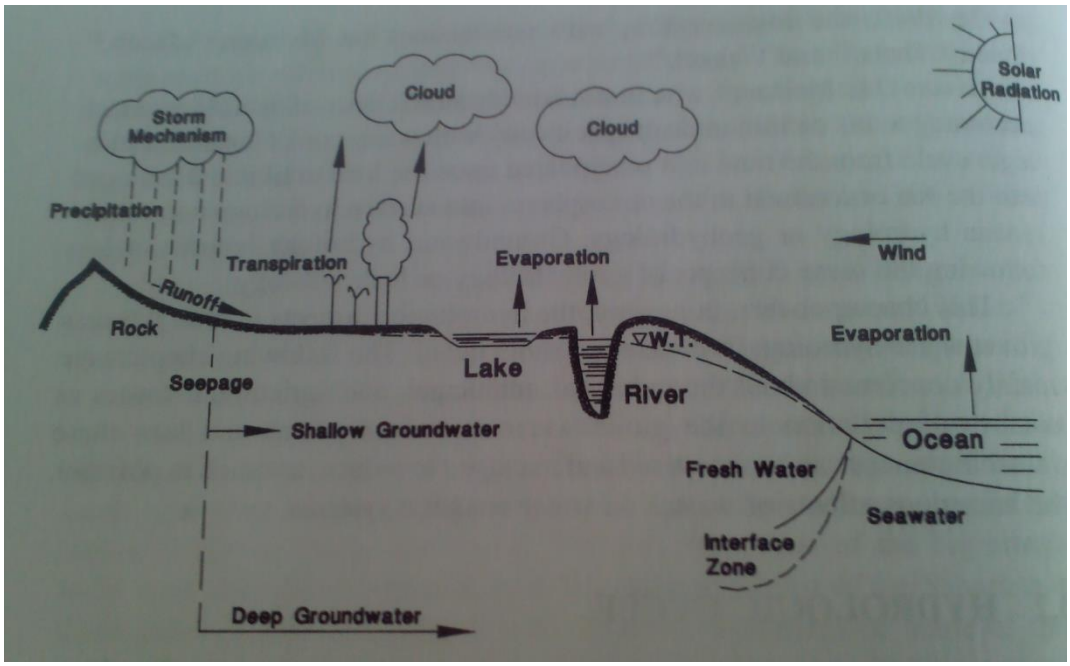


Figure 3. Hydrologic cycle. [8]

Contaminants can be introduced into water from various sources throughout the hydrologic cycle. Contaminants may be diluted, concentrated, or carried through the cycle with the water. Source water quality management seeks to minimize contaminant input to water resources used as sources of drinking water. [7, p.190]

4.1 Water sources

The most common type of water source, which is being used by humans, is fresh water. The main reason is that the total concentration of dissolved constituents is low in freshwater, whereas seawater contains high concentrations of dissolved constituents.

Freshwaters are naturally derived from surface sources such as lakes, rivers, and glaciers, and groundwater aquifers. There are many differences between surface and groundwater; they are going to be treated in more detail in chapter 5 below. However, the most significant differences, which are responsible for the different quality and treatment of the two types of water, are that surface water is turbid, which is caused by the presence of clays and other light particles that may be in there; thus, treatment for the removal of turbidity is usually necessary prior to uses other than irrigation, in contrast, groundwater often has higher concentrations of total dissolved solids, which may

be caused by the mineral pickup from soil and rocks. Many ground waters are noted for high concentrations of particular ions and elements such as calcium, magnesium, boron, and fluoride. Due to the fact that ground waters have usually higher quality for consumption than surface waters and they do not need as much treatment, they are often preferred as more suitable sources of water for small communities like villages or islands. Surface waters, on the other hand, are usually preferred from large communities such as big cities or capital cities because of their reliability. [9, p.6]

4.1.1 Surface water sources

As it has been already mentioned above, surface water is the term used to describe water on the land surface. This type of water, on the land surface, is produced by runoff of precipitation and by groundwater seepage. Surface water may be running, as in streams, rivers, and brooks, or quiescent, as in lakes, reservoirs, impoundments, and ponds. For regulatory purposes, surface water is defined as all water open to the atmosphere and subject to surface runoff. [7, p.190] Figure 4 presents the river Mornos, which is one of Athens' drinking water sources.

Figure 4. Surface water source for drinking water in Central Greece. [10]

After surface water has been produced, it follows the path of least resistance. A series of brooks, creeks, streams, and rivers carries water from an area of land surface that slopes down toward one primary water course. This drainage area is known as a watershed or drainage basin. A watershed is a basin surrounded by a ridge of high ground that separates one drainage from another. [7, p.190]

Source water quality is highly influenced by the point within the watershed where water is diverted for treatment. The quality of streams, rivers, and brooks will vary according to seasonal flow and may change significantly because of precipitation and accidental spills. Lakes, reservoirs, impoundments, and ponds typically have less sediment than rivers but are subject to greater impacts from microbiological activity than river sources. Surface water's quality is of great importance for human health and ecological systems, especially around urban areas due to the fact that rivers, and their tributaries passing through cities receive a lot of contaminants from industrial, domestic/sewage, and agricultural effluents. Quiescent water bodies, whether natural or human-made, are living ecosystems. Each is unique and changes in character from year to year. In addition, water bodies, including source water lakes and reservoirs, age over a relatively long period of time as a result of natural processes. This aging process is caused by micro-

biological activity that is directly related to the nutrient levels in the water body and can be accelerated by human activity. [7, p.190; 22, p.30]

4.1.2 Groundwater sources

Water that lies beneath the ground surface is referred to as underground or subsurface water. Groundwater is that portion of subsurface water which occupies the part of the ground that is fully saturated and flows into a hole under pressure greater than atmospheric pressure. Underground water occurs in two different zones, which are presented in Figure 5. One zone is immediately below the land surface where the soil and rock contains both water and air, and is called unsaturated zone. The unsaturated zone is almost invariably underlain by a zone in which all interconnected rock openings are full of water, this zone is called saturated. Water in the saturated zone is the only underground water that is available to supply wells and springs, and it is the only water to which the name groundwater is correctly applied. Recharge of the saturated zone occurs by percolation of water from the land surface through the unsaturated zone. [7, p.190; 11, p.1007]

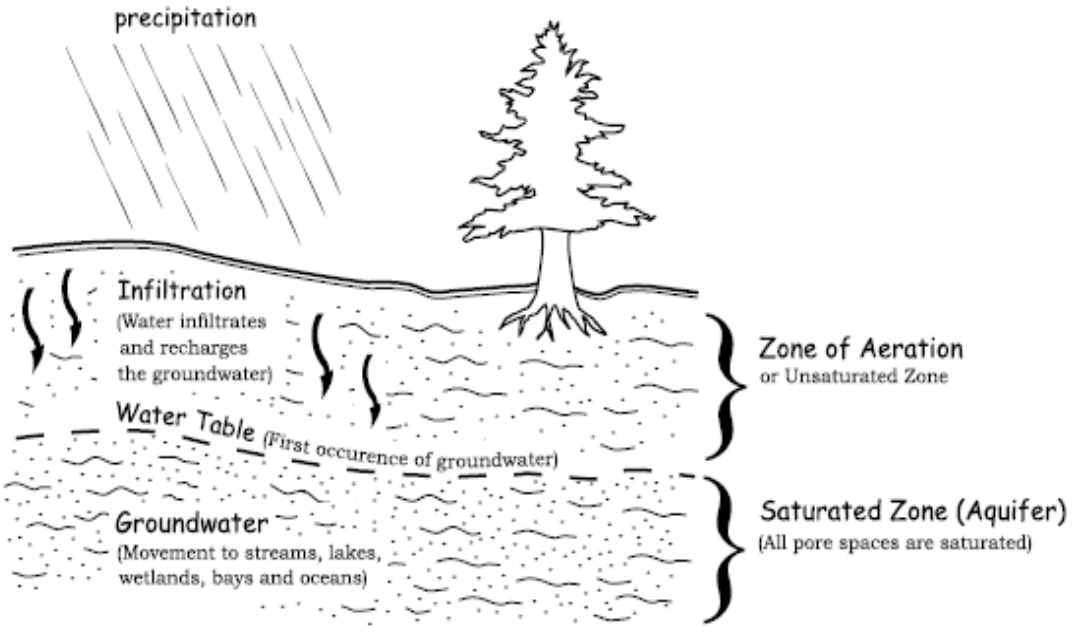


Figure 5. Different zones of groundwater. [12, p.2]

All rocks that underlie the earth's surface can be classified either as aquifers or as confining beds. An aquifer is a body of saturated rock or sediment through which water can

move easily to end up to a well or spring. A confining bed is a rock unit having very low hydraulic conductivity that restricts the movement of groundwater either into or out of adjacent aquifers. [7, p.190]

Some groundwater sources may be subject to contamination from surface waters. Springs, infiltration galleries, shallow wells, and other collectors in subsurface aquifers may be hydraulically connected to nearby surface water sources, depending on local geology. For regulatory purposes, these sources are referred to as ground waters ‘’under the direct influence of surface waters.’’ Groundwater contains a wide variety of dissolved chemical components in various concentrations as a result of the reactions between groundwater and the surrounding aquifer material. Temperature changes can cause alteration of groundwater chemistry due to the fact that temperature is a considerably important factor in the solubility of minerals, reactions kinetics, oxidation of organic matter, redox processes, and sorption-desorption of anions and cations. [7, p.190; 11, p.1007; 23, p.22]

4.2 Water use and resources

Fresh water is substantial for human life. Even though the percentage of fresh water that is available for consumption and use on earth is approximately 1%, it is, however, enough for everyone’s needs.

In Europe, by the year 2005, 38% of the abstracted water was used for agricultural purposes, 18% for domestic uses, 11% for industry purposes, and 33% for energy production. However, as expected, there are many differences between all the member States of European Union. For example, in more southern countries such as Cyprus, Malta, and Turkey, almost 80% of the abstracted water is used for agriculture, while in Portugal, Greece, Spain, France, and Italy approximately 46% of the abstracted water is used for this purpose. In the central and northern countries such as Austria, Belgium, Finland, UK, and Scandinavia, less than 5% of the abstracted water is used for agriculture, while more than 50% is used for energy production due to weather conditions. [13]

From all European Member States, Nordic countries have the highest water resources per capita, while Malta, Cyprus, and some densely populated European countries such

as Germany, Poland, Spain, and England have the lowest water availability per capita. There are thirteen countries that have less than 5,000 m^3/capita/year of water resources. [13]

	Groundwater abstraction			Surface water abstraction		
	2001	2006	2011	2001	2006	2011
Belgium (1)	679	645	618	6 316	5 800	5 558
Bulgaria	719	647	545	5 114	5 930	5 840
Czech Republic	529	379	378	1 310	1 557	1 508
Denmark (2)	693	671	649	15	5	5
Germany (3)	6 204	6 033	:	31 802	29 524	:
Estonia	272	237	299	1 199	1 324	1 575
Ireland (4)	:	:	213	:	:	517
Greece (4)	3 390	3 679	3 651	6 384	5 768	5 820
Spain (2)	5 759	6 398	6 595	30 349	27 701	26 949
France (2)	6 284	6 184	6 143	27 261	26 368	26 968
Croatia	:	464	521	:	:	637
Italy	:	:	:	:	:	:
Cyprus	141	140	155	61	93	66
Latvia (2)	116	102	270	141	107	105
Lithuania	157	180	175	2 611	1 901	457
Luxembourg	:	:	22	:	:	24
Hungary (5)	726	541	506	:	:	4 926
Malta (2)	36	33	38	0	0	0
Netherlands (2)	977	1 045	1 008	7 938	9 934	9 659
Austria	:	:	:	:	:	:
Poland	2 700	2 831	2 733	8 899	9 576	9 178
Portugal	:	366	:	:	550	:
Romania	990	650	600	6 353	4 680	5 992
Slovenia	:	190	185	:	718	666
Slovakia	423	368	334	716	395	259
Finland	285	264	:	:	6 298	:
Sweden (2)	628	346	348	2 048	2 285	2 342
United Kingdom (6)	2 366	2 266	2 159	7 872	7 005	5 523
Iceland	159	:	:	5	:	:
Switzerland	:	1 255	:	:	961	:
FYR of Macedonia (1)	62	134	162	606	766	885
Serbia	72	545	499	2 510	3 248	3 683
Turkey	10 670	11 882	13 560	33 780	31 836	:
Bosnia and Herzegovina	:	150	148	:	178	182

(1) Data for 2009 instead of 2011.
(2) Data for 2010 instead of 2011.
(3) Data for 2004 instead of 2006.
(4) Data for 2007 instead of 2011.
(5) Data for 2008 instead of 2011.
(6) England and Wales only.

Figure 6. Surface water and groundwater abstraction in years 2001-2011. [14]

Figure 6 presents data about abstraction quantities of surface water and groundwater in years 2001-2011 in EU countries. It can be concluded on the basis of the figure that

in Finland, the amount of abstracted surface water is bigger than the abstracted amount of groundwater, while in Greece, the amount of abstracted groundwater is bigger than that of surface water's abstraction.

In Greece, the total freshwater availability is about 3,209 hm^3 and consists of 2,596 hm^3 surface water and 613 hm^3 groundwater; this means that approximately 80-85% of freshwater resources are in form of surface water and the rest 15-20% are groundwater. The consumption of fresh water per capita is around 830 m^3 with peaks recorded during heat wave days as it is expected and during days of intensive snow fall, usually in the southern regions. [15]

Figure 7 shows the annual water availability in Greece.

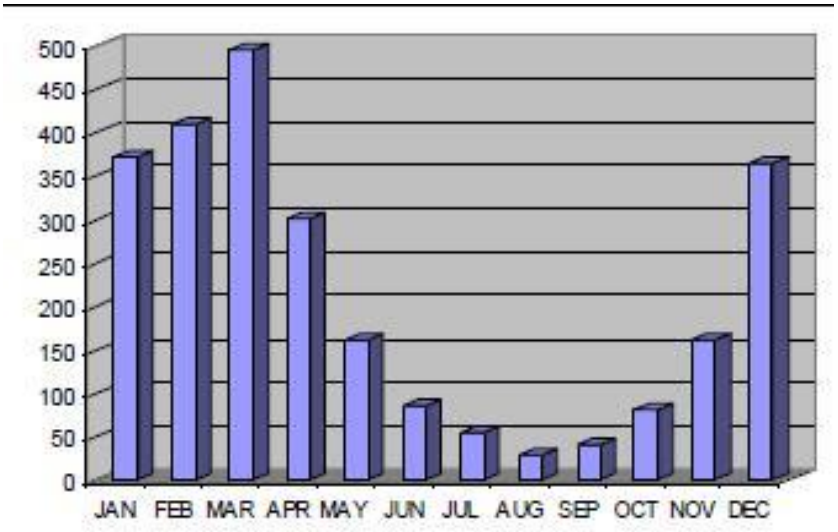
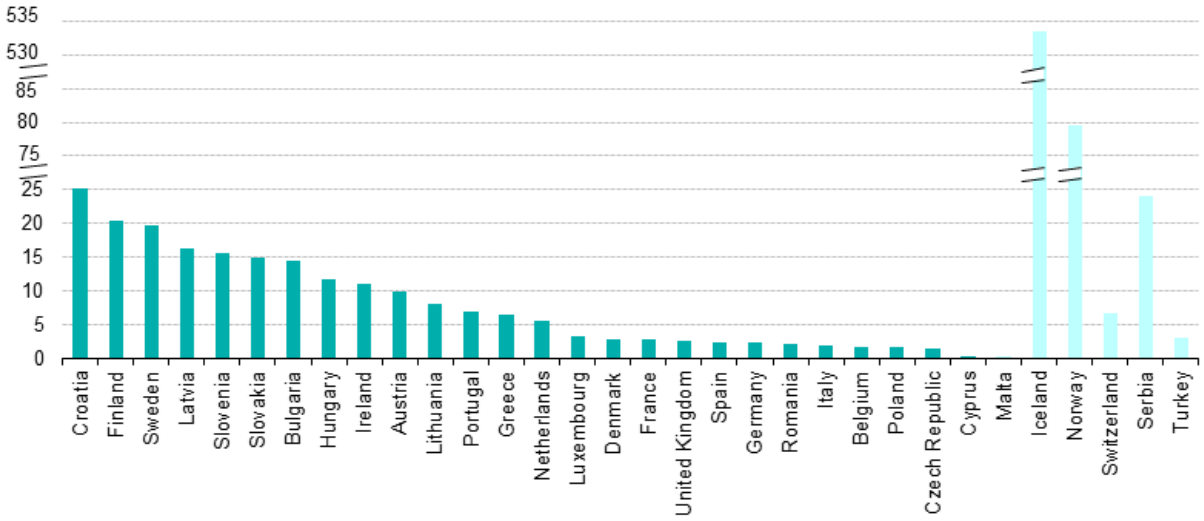


Figure 7. Annual water availability in Greece. [15]

It is widely known that summer in Greece might be extremely warm, which explains the low water availability in these warm months of the year. From the figure it can be also noticed that March exhibits the highest water availability, which may also mean that this specific month is one of the coldest months in Greece.

Finland is completely self-sufficient in terms of groundwater and would have a lot of capacity for export. There are 6,350 groundwater areas, and they form 5.4 million cubic meters of groundwater every day. In Finland, the amount of all groundwater which is being used is only 10%. Approximately 60% of the water distributed by public waterworks is groundwater and the remaining 40% is surface water. [16]

Figure 8 below presents freshwater resources per inhabitant in Europe, as Eurostat publishes them.



(1) The minimum period taken into account for the calculation of long term annual averages is 20 years.
Population data are as of 1 January 2011; Estonia, not available; Ireland and Turkey, estimates.

Figure 8. Freshwater resources per inhabitant. [14]

As it can be noticed in Figure 8 Finland has more freshwater resources than Greece, which is due to Finland's vast water area and high water availability. Also each country's weather conditions have significant impact on fresh water resources.

4.2.1 Water use in Greece

Irrigation accounts for a major proportion of water use in Greece, while domestic use in different regions ranges from 3 to 66%, and industrial use covers 0.2 to 16% of the total water abstraction (Figure 9). The increased demand for water, either for urban or agricultural use, cannot be always met despite adequate precipitation. Water imbalance is often experienced, especially in the coastal and south-eastern regions, due to temporal and spatial variations of the precipitation, the increased water demand during the summer months, and the difficulty of transporting water through the mountainous terrain. However, on an average, there is a relatively high per capita water availability, i.e. around 5,800 m³/inh./yr. Even though this is lower than the corresponding figures for most European countries, it is much higher than that of other Mediterranean regions such as North Africa and Eastern Mediterranean countries. [15]

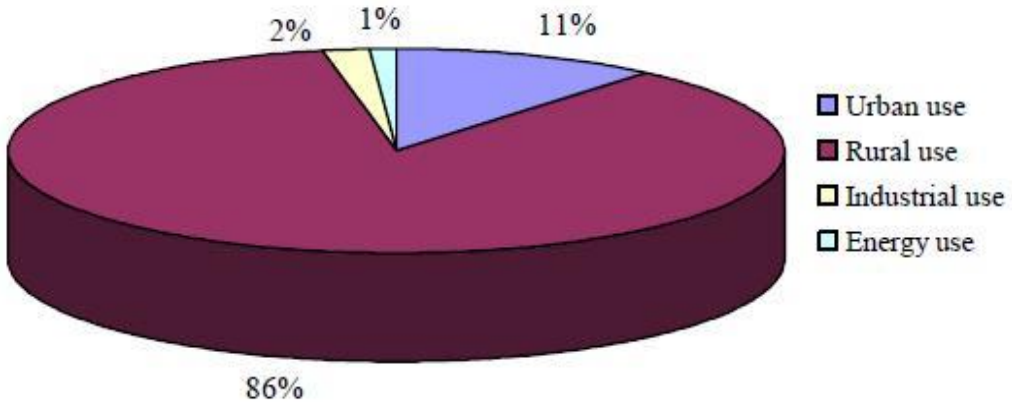


Figure 9. Water use in Greece. [15]

4.2.2 Water use in Finland

According to Figure 10, which is presented below, approximately 50% of freshwater is used for cooling and energy production in general, 30% is used for industry purposes, 18% is used for urban purposes, and almost 2% is used for agriculture. [17]

More specifically, the amount of water pumped by water works was 408 million m³/year, water consumption of communities per connection 242 l/day, and water abstraction by the industrial sector was 9,500 million m³/year. [17]

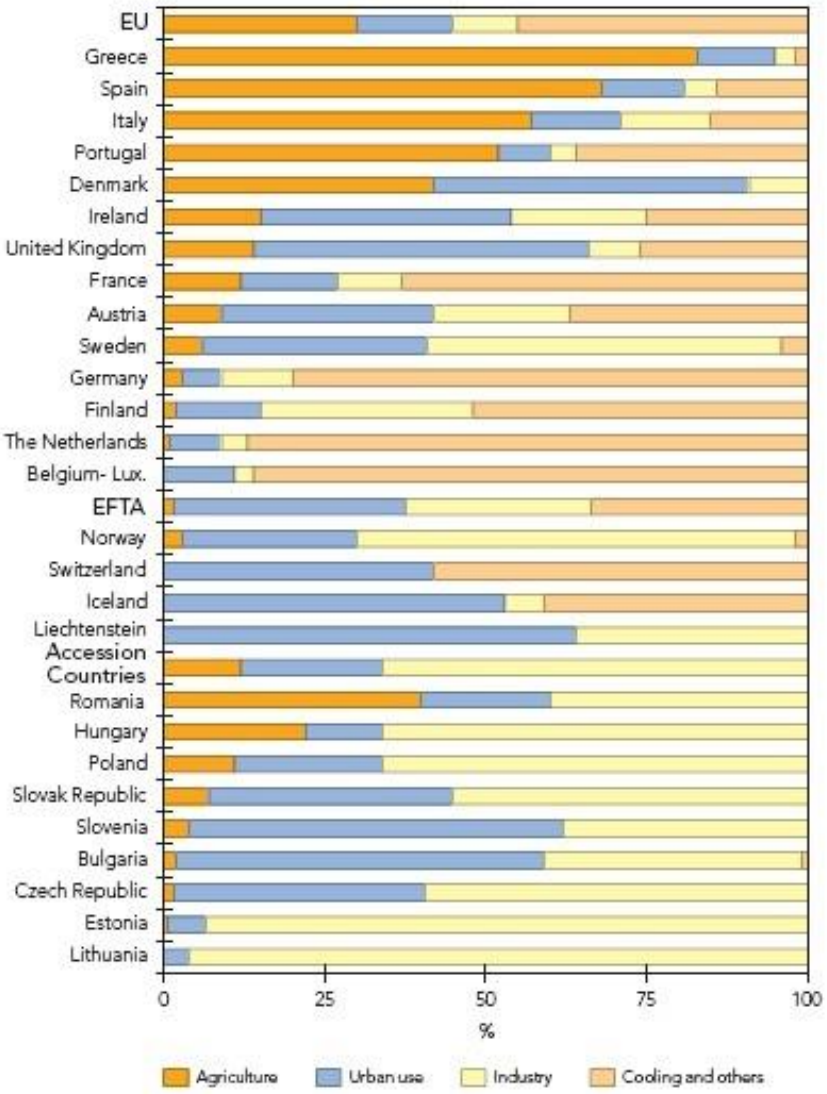


Figure 10. Water use by category in the EU countries. [15]

It can be seen in Figure 10 above that a major proportion of Finland's water is used for energy production due to the cold weather, whereas in Greece most of the water is used for irrigation due to the fact that agriculture is extremely important for the country's economy.

4.2.3 Water resources in Greece

The groundwater potential in Greece is around 10,300 million m^3/year, whilst 7,400 million m^3/year is karst groundwater. Various analyses of groundwater have shown that nitrate and ammonium exceed, in some cases, the critical value for drinking water; as a

consequence the Thessalic plain is designated as a vulnerable zone, according to the criteria of 91/676/EC Directive. [15]

However, many measures have been taken to improve the quality of groundwater, such as measures to reduce overall inputs of nitrogen to agriculture in the form of fertilizer and organic manures. [15]

In Greece, the mean annual surface run-off of mainland rivers is 35 billion cubic meters. More than 80% of the surface flows originates in eight major river basins: Acheloos (Central Greece), Axios, Strimonas and Aliakmonas (Macedonia), Evros and Nestos (Thrace), and Arachtos and Kalamas (Epirus). The largest lakes are Trichonida, Volvi and Vegoritida. The number of Greek wetlands, according to the inventory of Greek Biotope/Wetland Centre (or EKBY by its Greek initials), rises to about 400. Forty-one natural lakes, from which 19 have a size of over 5 km^2, occupy more than 600,000 hectares or 0.5% of the country's total area. The 14 artificial lakes, from which 10 have a size of over 5 km^2, occupy 26,000 hectares; hence, natural and artificial lakes occupy approximately 626,000 hectares of the country's total area. [15]

Surface water in the Aegean islands in the form of permanent drainage is something almost unknown, apart from a few exceptions. The main reasons that make surface water runoff occasional are the small area of the basin, the large gradients drainage, the limited grassing, and the limited spontaneous discharges. The largest drainage basin in the islands of the Aegean Sea (except for Crete) is Gadouras in Rhodes with an area of approximately 61 km^2. In the area of Cyclades, the most significant basin concerning the size is Melanes of Naxos. The average size of the main basins in the Cyclades does not exceed the 10 km^2. [15]

Table 4. Comparison between the size of the main basin and the whole size of the island. [15]

Km^2	Rhodes	Milos	Karpathos	Kalymnos	Kea	Paros	Kythnos	Antiparos
Islands' size	1398	150	301	110	130	194	99	35
Size of main basin	61	25	12	20	17	12	8	3.5
Fraction of island's size	1/22	1/6	1/25	1/5	1/7	1/16	1/12	1/10

Table 4 gives the sizes of some Greek islands and the size of the main basin in each island. Also, a comparison between the size of the main basin and the whole size of the island is made.

4.2.4 Water resources in Finland

Finland's water area contains 187,888 lakes and ponds with the length of more than five hundred square meters, as well as a total of 25,000 kilometers of rivers. The total area of Finland waters is some 10% of the total area of the country. The largest lake is Lake Saimaa with a surface area of 4,380 square km. The number of lakes and ponds larger than 0.0005 square km is 188,000, while the number of lakes larger than 0.01 and 100 square km is 56,000 and 47, respectively. [17;18]

Total river flow is 3,300 m³/s. The largest rivers in Finland are the river Vuoksi and the river Kemijoki with an average flow of 610 m³/s. [18]

The total freshwater resources available in Finland are 20,700 m^3 per capita as presented in Figure 11 below.

Water resources and water exploitation

	Total fresh water resources, long term annual average, thousand m^3 per capita*	Water exploitation index**, %
Belgium	1.9	32
Bulgaria	14.1	6
Czech Republic	1.5	12
Denmark	3.0	4
Germany	2.3	19
Estonia	9.2	15
Ireland	10.7	2
Greece	6.4	13
Spain	2.4	30
France	2.9	17
Italy	2.9	:
Cyprus	0.4	64
Latvia	14.9	1
Lithuania	7.3	9
Luxembourg	3.3	:
Hungary	11.6	5
Malta	0.1	21
Netherlands	5.4	11
Austria	10.1	:
Poland	1.7	18
Portugal	6.9	:
Romania	10.5	3
Slovenia	15.8	3
Slovakia	14.8	1
Finland	20.7	:
Sweden	19.8	1
United Kingdom***	2.9	13
Iceland	532.3	0
Norway	81.1	:
Switzerland	6.9	5
Turkey	3.3	:

* Long term annual average: a minimum 20 years of latest available data. For Malta average based on 1995-2007. Population data: 2008.
** The water exploitation index represents total water abstracted as a percentage of total freshwater resources. Reference period varies between countries: 2002 data: Hungary, 2004 data: Denmark, Germany; 2005 data: Belgium, Poland, Iceland; 2006 data: Spain, France, the Netherlands, the United Kingdom and Switzerland. 2007 data: other countries.
*** Includes England and Wales for the water exploitation index
: Data not available

Figure 11. Water resources and their exploitation. [19, p.2]

The water plants in Finland deliver over 1.1 million m^3 water daily, and the households consume 3/5 of the water. About 60% or 0.7 million m^3/day of the water is groundwater or artificial groundwater. Supply networks of water plants cover about 90% and sewage networks about 80% of Finnish households. [17;20]

At the beginning of 1970s, the share of groundwater was only 30%, but in 2001, approximately 61% of total public water undertakings and water abstraction was groundwater or artificial groundwater. There are nearly 1,500 groundwater sources of the total 1,560 individual water sources that exist in the country. [17]

In the coastal areas, the amount of available good quality groundwater is often limited. To serve these areas, several water supply systems using artificial groundwater have been constructed. [17]

Surface water is used mainly in some larger cities. The number of surface water sources is only about 70, but they represent 42% of the distributed water. For instance, about one million people in the Helsinki metropolitan area use water from Lake Päijänne. Raw water is conveyed in a 120 km long rock tunnel from the lake to Helsinki metropolitan area. [17;20]

5 Differences between groundwater and surface water

Surface water and ground water are two completely different sources of water, as it has already been explained above in chapter 4. In this chapter some of the differences between the two types of water are presented.

Surface water is easy to abstract from rivers, lakes or reservoirs by direct pumping. Water that has been abstracted from a surface water source can be treated after use and led back into a river. Dams and reservoirs can be used for hydroelectric power generation. Reservoirs can be used for recreation and other purposes. On the other hand, surface water has to be treated prior to use. The volume of water in rivers varies and water loss occurs through evaporation. It requires construction of expensive and environmentally damaging dams. It requires flooding of land for reservoirs. Reservoirs will eventually silt up. Construction of dams and reservoirs may trigger earthquakes. Sufficient rainfall and a large river catchment are required- there is no backup in drought conditions. [21, p. 166]

In addition to surface water, groundwater gets naturally filtered and purified as it percolates downward through the rocks. There is no loss of water through evaporation and no requirement for expensive and environmentally damaging dams. If the water comes from an artesian basin, the pumping costs will be low. On the other hand, it requires sedimentary rocks and presence of aquifers. There is the problem of surface subsidence. Pollutants have a long residence time. Pumping costs are high as water has to be raised vertically. Groundwater is not always suitable for drinking due to the presence of dissolved salts making the water brackish. [21, p. 166]

EXPERIMENTAL PART

6 Materials and Methods

The samples to be analyzed were tap water from Rhodes, Greece and Helsinki, Finland.

First, the two different water samples' basic parameters such as, pH, hardness, conductivity, anions (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}), cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), total dissolved solids (TDS), carbonates and bicarbonates, were measured repeatedly to identify the quality and the basic differences between these two waters. Each samples' measurement was repeated 8 times.

When the differences and the quality of the two water samples were identified, different solutions of each water sample were made, where various amounts of ammonium were added. Then all the solutions were measured by Hach spectrophotometer to determine ammonium's fate on the sample's matrix based on the results.

6.1 Sampling

The water sample from Finland was collected from the area of Roihuvuori in Helsinki. Four bottles were filled with tap water and transferred to the General Chemical State Laboratory of Rhodes, where the project was carried out. Each bottle had a volume of 1,5 l which means that the total amount of the sample was 6 l. After the bottles were transferred to the laboratory, they were emptied into a large container in order to mix the water sufficiently. The sample from Helsinki was stored in a container in a room protected from the sun, with normal room temperature.

The water sample from Greece was collected from the area of Plateia Haritou Gavriil in Rhodes. A large container was filled with 10 l of tap water. The sample from Rhodes was stored in a container in the same room where the sample from Helsinki was stored.

6.2 Determination of pH

Samples' pH was measured according to method APHA 4500-H B. For this method the equipment that was used was a HACH HQ40d multi pH- and conductivity-meter. Four measurements were done in the same day, and the other four were done after two days.

6.3 Determination of hardness

Samples' hardness was measured according to method APHA 2340 C.

The materials needed for this titrimetric method are Titriplex - Solution B (Merck, Germany), Idranal indicator buffer tablets for complexometry (Riedel – de Häen, Germany), and ammonium hydroxide solution (Fluka, Riedel - de Häen, Germany).

For this method, 100 ml of water sample were poured into a conical flask where one tablet of Idranal and 1 ml of ammonium hydroxide solution were added and dissolved into the sample by sufficiently agitating. When the tablet was added, the sample got a light red color. When the sample was ready and light red colored, the titration was started by pouring slowly drops of Titriplex – Solution B and simultaneously agitating till the sample turned green. Four measurements were done in the same day, and the other four were done after two days.

6.4 Determination of conductivity

Samples' conductivity was measured according to method APHA 2510 B. For this method the equipment that was used was a HACH HQ40d multi pH- and conductivity-meter. Four measurements were done in the same day, and the other four were done after two days.

6.5 Determination of F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-} anions

Samples' anions were measured using an in-house method by ion chromatography, based on APHA 4140 and ELOT EN ISO 10304.01:2007. The equipment employed consisted of two 732 IC Detectors (Metrohm), two 709 IC pumps (Metrohm), 830 IC Interface, 753 Suppressor Module (Metrohm). Four measurements were done in the same day, and the other four were done after two days.

6.6 Determination of Na^+, K^+, Ca^{2+}, Mg^{2+} cations

Sample's cations were measured using an in-house method by ion chromatography, based on APHA 4140 and ELOT EN ISO 10304.01:2007. The equipment employed consisted of two 732 IC Detectors (Metrohm), two 709 IC pumps (Metrohm), 830 IC Interface, 753 Suppressor Module (Metrohm). Four measurements were done in the same day, and the other four were done after two days.

6.7 Determination of Total Dissolved Solids

Samples' TDS were measured first by taking the weight of the beaker. Then, the beaker was placed into an 180 °C oven for one hour. After that, it was placed in a drier for 40 minutes. Next, the sample was poured into the oven till the water evaporated. Finally, the sample was placed in a drier again for approximately 40 minutes and its weight was measured. The standard method used for this measurement was APHA 2540 C. Four measurements were done in the same day, and the other four were done after two days.

6.8 Determination of carbonates and bicarbonates

Samples' carbonates and bicarbonates were measured by placing 100 ml of samples into a beaker and measuring it with 888 Titrado (Metrohm). The method used was APHA 2320. Four measurements were done in the same day, and the other four were done after two days.

6.9 Addition of ammonium

Six standard solutions were made for the calibration of the equipment. In each one solution was added a specific amount of ammonium standard for IC to reach the following concentrations: 0.15 mg/l, 0.5 mg/l, 1 mg/l, 1.5 mg/l, 2 mg/l and 2.5 mg/l.

Each standard ammonium solution was measured with Hach DR 2000 direct reading spectrophotometer three times and one blank sample without ammonium addition.

After the calibration six solutions, which contained a specific amount of ammonium, were made with standard addition method for each water sample. The concentrations were the same as in the standard solutions, which were: 0.15 mg/l, 0.5 mg/l, 1 mg/l, 1.5 mg/l, 2 mg/l and 2.5 mg/l, and each solution was measured again with Hach DRI 2000 direct reading spectrophotometer five times and one blank sample without ammonium addition.

For this method, the materials needed are Nessler reagent (Hach, USA), polyvinyl alcohol dispersing agent (Hach, USA), and mineral stabilizer (Hach, USA).

Each measurement was performed by filling a 25-ml graduated cylinder to the 25-ml mark with sample and another 25-ml graduated cylinder with demineralized water (blank). Then, by adding three drops of mineral stabilizer and three drops of polyvinyl alcohol dispersing agent to each cylinder and by inverting several times to mix. Then by pipetting 1 ml of Nessler Reagent to each cylinder and by waiting 1 minute for it to react, and then by pouring each sample into the cells and measuring them with the spectrophotometer.

7 Results

7.1 pH results

The results from pH analysis regarding Rhodes's and Helsinki's water samples are presented in Table 5.

Table 5. Rhodes's and Helsinki's water samples' pH results.

Measurement's no.	Rhodes samples	Helsinki samples
	pH	pH
1	7.7	7.7
2	7.7	7.7
3	7.7	7.7
4	7.7	7.7
5	7.7	7.7
6	7.7	7.7
7	7.7	7.7
8	7.7	7.7

Samples have been measured at 25 °C.

7.2 Hardness

The results of Rhodes's and Helsinki's water samples' hardness analyses are presented in Table 6.

Table 6. Rhodes's and Helsinki's water samples' hardness results.

Measurement's no.	Rhodes samples	Helsinki samples
	Hardness (mg/l $CaCO_3$)	Hardness (mg/l $CaCO_3$)
1	287	54
2	288	55
3	289	55
4	289	54
5	284	55
6	285	54
7	286	54
8	286	54

The quantity of Titriplex solution that was used till the color of the sample turned green had to get multiplied by 17.857 to receive the right results, which are presented above in Table 6.

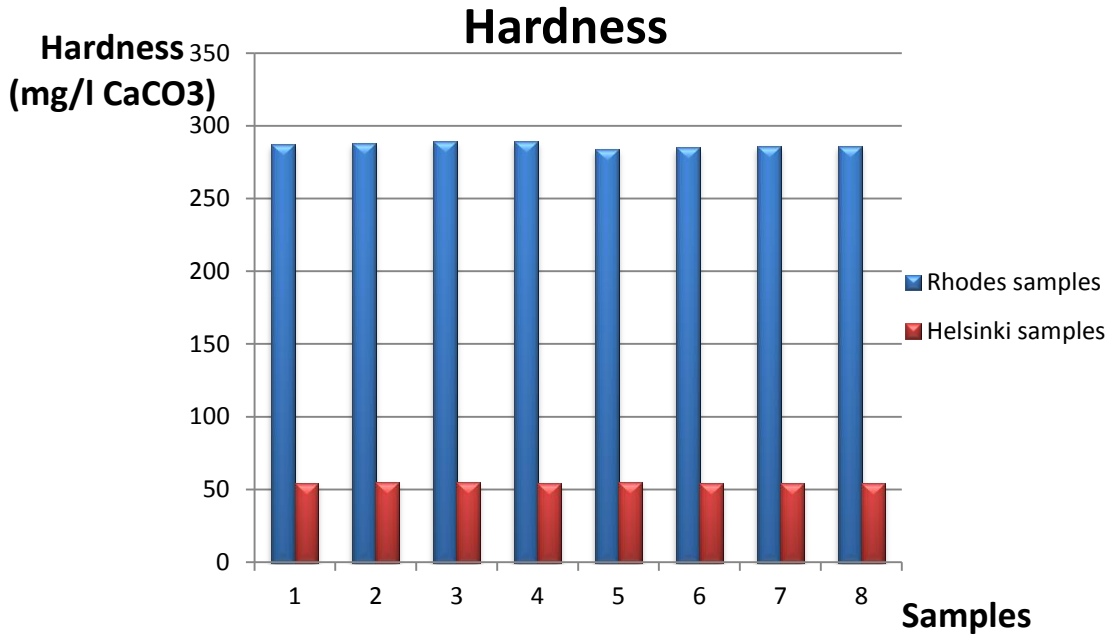


Figure 12. Rhodes's and Helsinki's water samples' hardness results.

The results of hardness measurements are presented above in Figure 12.

7.3 Conductivity

The results of Rhodes's and Helsinki's water samples' conductivity analyses are presented in Table 7 below.

Table 7. Rhodes's and Helsinki's water samples' conductivity results.

Measurement's no.	Rhodes samples	Helsinki samples
	Conductivity (µS/cm)	Conductivity (µS/cm)
1	651	154.5
2	649	153.7
3	652	153.3
4	649	153.4
5	656	153.3
6	656	154.1
7	658	153.6
8	657	153.6

Samples have been measured at 25 °C.

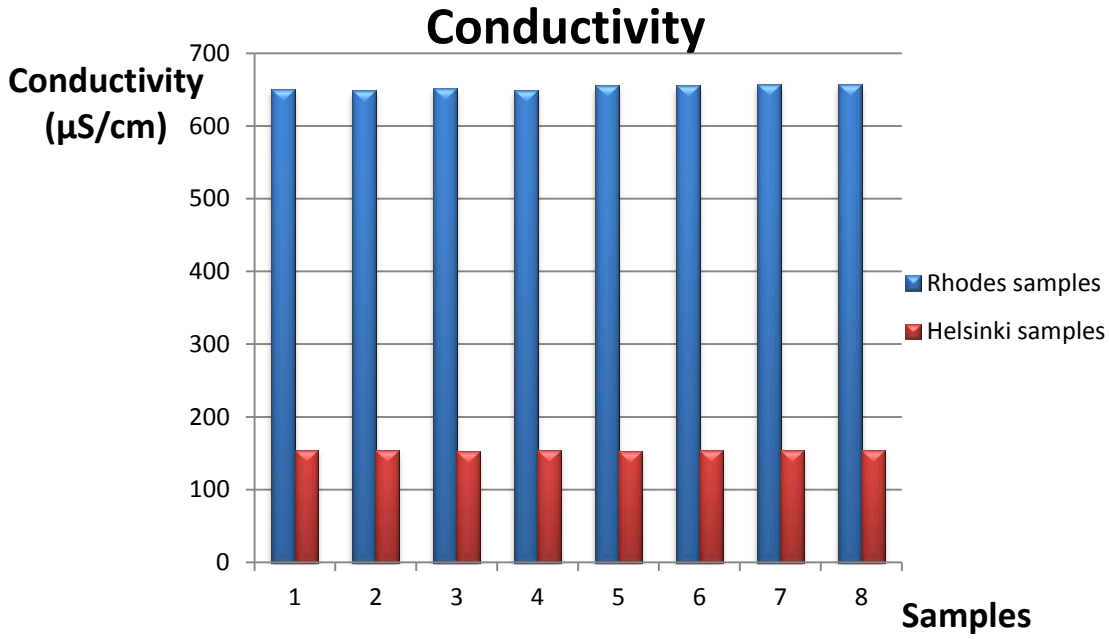


Figure 13. Rhodes's and Helsinki's water samples' conductivity results.

Conductivity results are presented graphically in figure 13 above.

7.4 F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-} anions

The results of anions determination are presented below in Table 8.

Table 8. Rhodes's and Helsinki's water samples' anions results.

	Rhodes samples	Helsinki samples
	Anions (mg/l)	Anions (mg/l)
F^-	<0.2	<0.2
Cl^-	35.8	<5.7
Br^-	<0.2	<0.2
NO_3^-	<5.7	<5.7
SO_4^{2-}	12.3	22.2

Minimum reporting level (MRL) means that if the result is lower that this specific reporting level, it is not needed to be mentioned exactly, instead, it is represented, for exam-

ple, as <0.2. The MRLs for anions are as follows: Fluoride 0.2, Chlorine 5.7, Bromide 0.2, Nitrate 5.7, and Sulfate 5.5.

7.5 Na^+, K^+, Ca^{2+}, Mg^{2+} cations

The results of cations determination are shown below in Table 9.

Table 9. Rhodes's and Helsinki's water samples' cations results.

	Rhodes samples	Helsinki samples
	Cations (mg/l)	Cations (mg/l)
Na^+	27.6	6.6
K^+	1.5	1.5
Ca^{2+}	42.3	3.3
Mg^{2+}	57.5	39

The MRL for cations is Magnesium 3.

7.6 Total Dissolved Solids

The results from the total dissolved solids analyses are shown below in Table 10.

Table 10. Rhodes's and Helsinki's water samples' TDS results.

Measurement's no.	Rhodes samples	Helsinki samples
	TDS (mg/l)	TDS (mg/l)
1	361	102
2	317	94
3	335	48
4	325	77
5	369	79
6	360	81
7	371	87
8	359	80

The results were received by deducting the weight before from the weight after and by converting the values into mg/l.

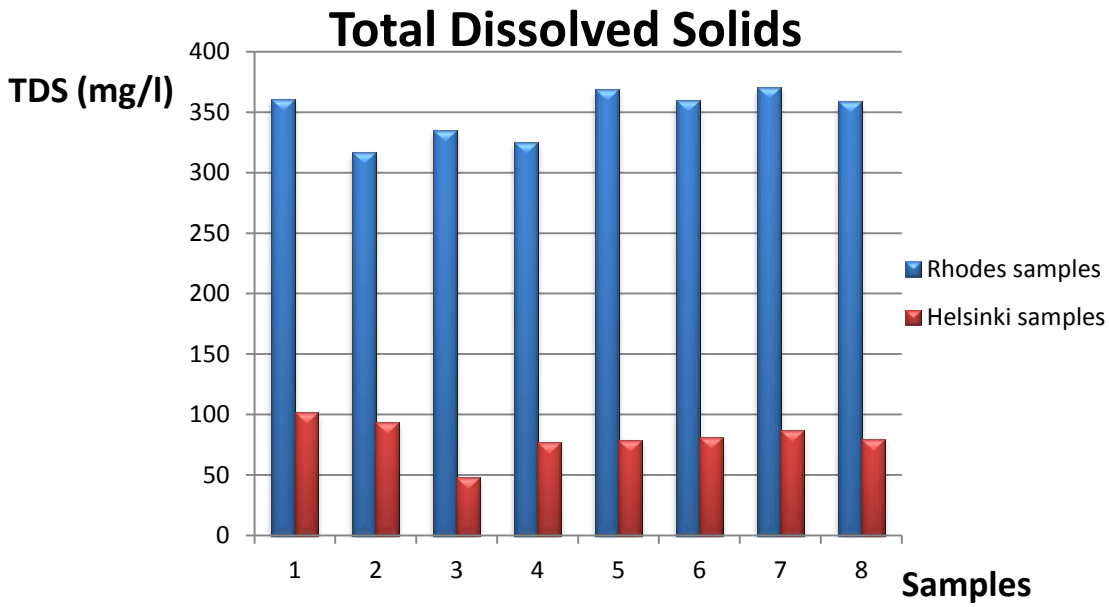


Figure 14. Rhodes's and Helsinki's water samples' TDS results.

TDS results are presented graphically in Figure 14 above.

7.7 Carbonates and bicarbonates

The results of carbonate and bicarbonate measurements are presented below in Table 11.

Table 11. Rhodes's and Helsinki's water samples' CO_3 and HCO_3 results.

	Rhodes samples		Helsinki samples	
Measurement's no.	CO_3 (mg/l)	HCO_3 (mg/l)	CO_3 (mg/l)	HCO_3 (mg/l)
1	0	334.0	0	51.1
2	0	337.5	0	51.8
3	0	334.9	0	55.5
4	0	335.4	0	47.2
5	0	336.4	0	47.6

6	0	334.6	0	53.9
7	0	336.6	0	47.0
8	0	339.7	0	66.5

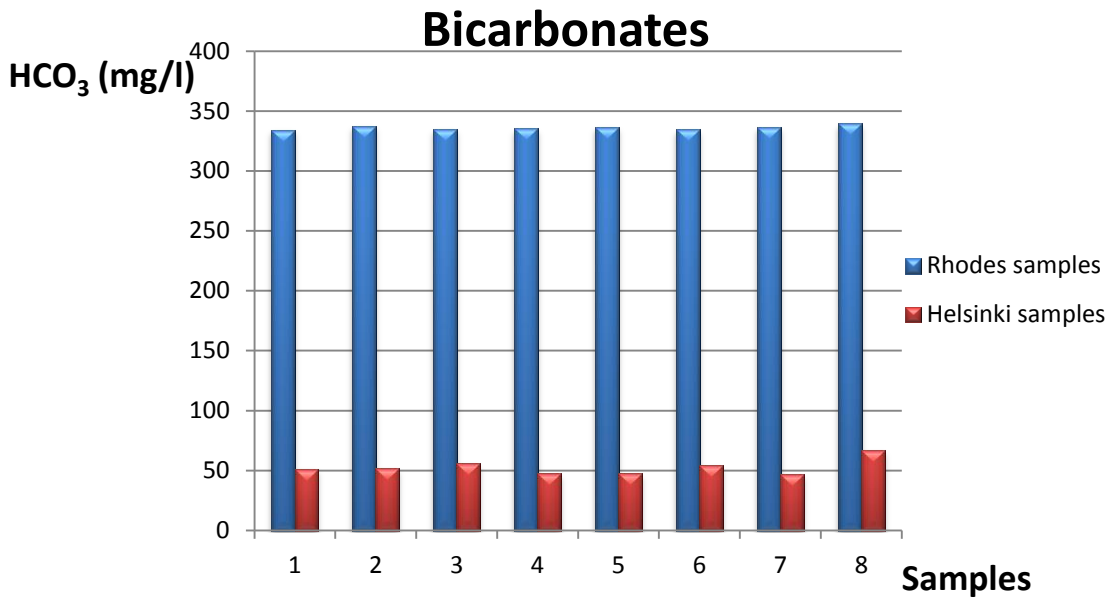


Figure 15. Rhodes's and Helsinki's water samples' HCO_3 results.

7.8 Ammonium addition results

In Table 12 below the average results of standard ammonium solutions' measurements are presented.

Table 12. Standard ammonium solutions' average results.

C (mg/l)	Standard ammonium solutions' average C (mg/l NH_4^+)
0.15	0.12
0.5	0.45
1	0.88
1.5	1.32
2	1.78
2.5	2.18

All the results that the spectrophotometer delivered were multiplied by 1.29 for them to be converted into mg/l NH_4^+.

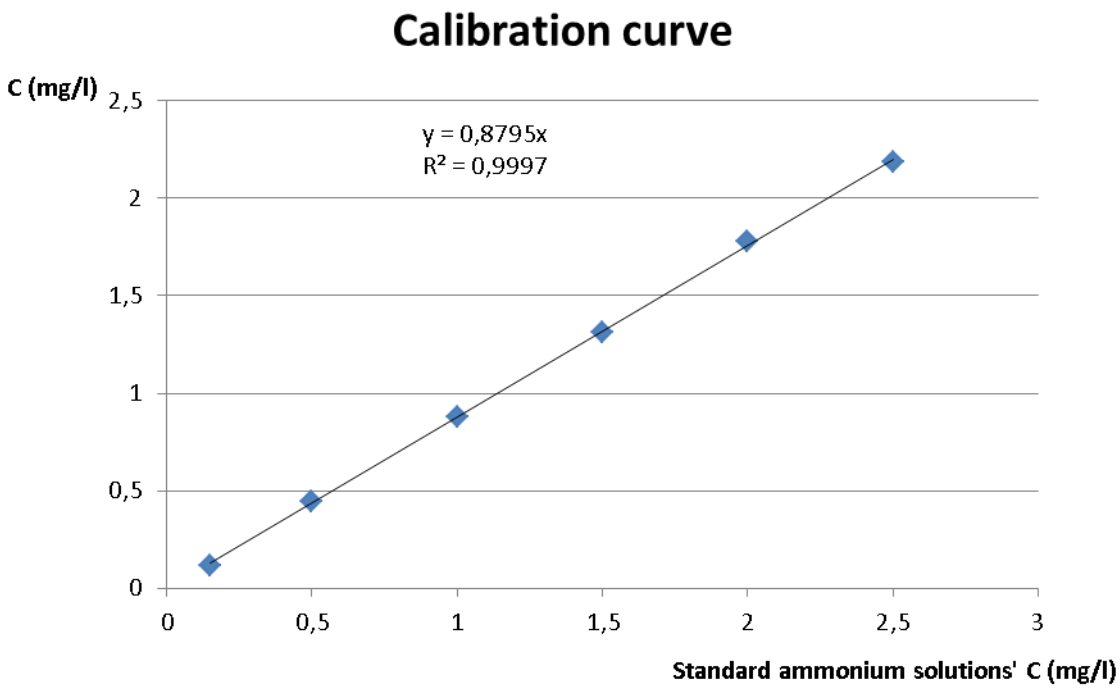


Figure 16. Calibration curve for the standard ammonium solutions.

Based on the average results of standard ammonium solutions' measurements, a calibration curve was designed, and is presented in the Figure above.

Table 13. Rhodes and Helsinki samples' ammonium addition's results.

Rhodes samples					
C (mg/l)	**Measured ammonium's C (mg/l NH_4)**				
0	0.03				
	1st measurement	2nd	3rd	4th	5th
0.15	0.15	0.14	0.18	0.18	0.15
0.5	0.44	0.48	0.52	0.44	0.44
1	0.93	0.92	0.92	0.94	0.93
1.5	1.5	1.48	1.48	1.39	1.38
2	1.9	1.91	1.91	1.81	1.79
2.5	2.37	2.37	2.37	2.21	2.23
Helsinki samples					
0	0.08				

0.15	0.23	0.25	0.25	0.23	0.23
0.5	0.55	0.54	0.54	0.52	0.52
1	0.99	1.01	1.03	1.06	1.03
1.5	1.46	1.46	1.44	1.61	1.5
2	1.97	2.01	1.99	1.9	1.9
2.5	2.41	2.41	2.41	2.37	2.35

The new and adjusted results based on the calibration curve, which are going to be used for the statistical analysis, are presented below in Table 14 and 16.

Table 14. Corrected results of ammonium's concentration in Rhodes' samples.

C (mg/l)	Corrected Rhodes samples' ammonium C (mg/l NH_4)					
	1st measurement	2nd	3rd	4th	5th	Average
0.15	0.15	0.14	0.18	0.18	0.15	0.16
0.5	0.47	0.52	0.56	0.47	0.47	0.50
1	1.03	1.02	1.02	1.04	1.03	1.03
1.5	1.68	1.66	1.66	1.56	1.54	1.62
2	2.13	2.14	2.14	2.03	2.01	2.09
2.5	2.67	2.67	2.67	2.48	2.51	2.60

Two additional measurements were made on the same solutions, one of which was done one day after the first measurements, and the other one after 7 days. The reason for these additional measurements was to observe ammonium's metabolism in the two samples' matrices. The results are presented below in Tables 15 and 17.

Table 15. Rhodes samples' measurements after one day and after seven days.

C (mg/l)	**Rhodes samples' ammonium C after one day (mg/l NH_4)**					
	1st measurement	2nd	3rd	4th	5th	Average
0.15	0.13	0.12	0.15	0.15	0.13	0.14
0.5	0.40	0.44	0.48	0.40	0.40	0.43
1	0.88	0.87	0.87	0.88	0.88	0.88
1.5	1.43	1.41	1.41	1.33	1.31	1.38
2	1.81	1.82	1.82	1.73	1.71	1.78
2.5	2.27	2.27	2.27	2.11	2.13	2.21
C (mg/l)	**Rhodes samples' ammonium C after seven days (mg/l NH_4)**					
0.15	0.05	0.04	0.05	0.05	0.05	0.05
0.5	0.14	0.16	0.17	0.14	0.14	0.15

1	0.31	0.31	0.31	0.31	0.31	0.31
1.5	0.50	0.50	0.50	0.47	0.46	0.49
2	0.64	0.64	0.64	0.61	0.60	0.63
2.5	0.80	0.80	0.80	0.74	0.75	0.78

In table 15 are presented the results of Rhodes samples' ammonium concentration after one and seven days.

Table 16. Corrected results of ammonium's concentration in Helsinki's samples.

C (mg/l)	Corrected Helsinki samples' ammonium C (mg/l NH_4)					
	1st measurement	2nd	3rd	4th	5th	Average
0.15	0.18	0.19	0.19	0.18	0.18	0.19
0.5	0.55	0.53	0.53	0.50	0.50	0.52
1	1.05	1.06	1.09	1.12	1.09	1.08
1.5	1.57	1.57	1.56	1.75	1.62	1.61
2	2.16	2.20	2.17	2.07	2.07	2.14
2.5	2.66	2.66	2.66	2.61	2.59	2.64

In table 16 are presented the adjusted results of ammonium's concentration in Helsinki's samples.

Table 17. Helsinki samples' measurements after one day and after seven days.

C (mg/l)	**Helsinki samples' ammonium C after one day (mg/l NH4)**					
	1st measurement	2nd	3rd	4th	5th	Average
0.15	0.17	0.18	0.18	0.17	0.17	0.18
0.5	0.52	0.50	0.50	0.8	0.48	0.49
1	1.00	1.01	1.04	1.06	1.04	1.03
1.5	1.49	1.49	1.48	1.66	1.54	1.53
2	2.05	2.09	2.06	1.97	1.97	2.03
2.5	2.53	2.53	2.53	2.48	2.46	2.51
C (mg/l)	**Helsinki samples' ammonium C after seven days (mg/l NH4)**					
0.15	0.14	0.15	0.15	0.14	0.14	0.15
0.5	0.44	0.42	0.42	0.40	0.40	0.42
1	0.84	0.85	0.87	0.90	0.87	0.86
1.5	1.26	1.26	1.25	1.40	1.30	1.29
2	1.73	1.76	1.74	1.66	1.66	1.71
2.5	2.13	2.13	2.13	2.09	2.07	2.11

Table 17 presents the results of Helsinki samples' ammonium concentration after one and seven days.

7.9 Statistical calculations of the results

The corrected results from Tables 14 and 16 were analyzed statistically by using F- and t-test, and also by calculating the u_{bias} value to examine the accuracy of the results.

For the F- and t- test, the following calculations had to be done:

Standard deviation's calculation was made by using Microsoft Excel's standard deviation formula. The results are presented in Table 18 below.

Table 18. Standard deviation.

	Standard deviation	
C (mg/l)	Rhodes samples	Helsinki samples
0.15	0.020	0.008
0.5	0.039	0.020
1	0.012	0.029
1.5	0.063	0.079
2	0.066	0.061
2.5	0.097	0.034

After standard deviation's calculation, variance s^2 was calculated by using the following formula:

$$s^2 = \frac{(n_1-1) \times s_1^2 + (n_2-1) \times s_2^2}{n_{1+}n_2-2}$$

The results are presented in Table 19 below.

Table 19. Variance s^2.

C (mg/l)	Variance s^2
0.15	3.00036
0.5	3.00155
1	3.00077

1.5	3.00816
2	3.00647
2.5	3.00843

Afterwards, F_{exp} and t_{exp} values were calculated by using the following formulas:

For t-test: $t_{exp} = \frac{x_1 - x_2}{\sqrt{s^2 \times (\frac{1}{n_1} + \frac{1}{n_2})}}$

Also, null and alternative hypotheses were established for both, t-test and F-test.

For t-test:

H_0: The matrix of the two samples was affected likewise.

H_A: The matrix of the two samples was not affected likewise.

The results are presented in Table 20 below.

Table 20. t_{exp} results.

C (mg/l)	t_{exp}
0.15	2.848
0.5	1.227
1	3.843
1.5	0.115
2	1.111
2.5	0.717

The tabulated value for d.o.f. n = 5 in each case, and a 1-tailed, 95% confidence level is t_{theor} = 2.776. All the values of t_{exp} are smaller than t_{theor} except for the values at the concentrations of 0.15 mg/l and 1 mg/l. Thus, null hypothesis is rejected, which means that the matrix of the two samples was not affected likewise.

For F-test: $F_{exp} = \frac{s_1^2}{s_2^2}$

Hypotheses for F-test:

H_0: Standard deviations are equal.

H_A: Standard deviations are not equal.

The results are presented below.

Table 21. F_{exp} results.

C (mg/l)	F_{exp}
0.15	6
0.5	4
1	5.42857
1.5	1.53476
2	1.17341
2.5	8.24528

The tabulated value for d.o.f. n = 5 in each case, and a 1-tailed, 95% confidence level is F_{theor} = 9.6. All of the values of F_{exp} are smaller than F_{theor}; thus, null hypothesis is accepted, and standard deviations are equal.

For the calculation of u_{bias}, for which the method of NORDTEST [25] was applied, the following formulas were used:

$U_{bias} = \sqrt{RMS_{bias}^2 + \frac{s_{bias}^2}{\sqrt{n}^2} + u_{(Cref)}^2}$, n=6

where, $RMS_{bias} = \sqrt{\frac{\sum error^2}{n}}$, n=6

and, $error_{(\%)} = \frac{C_{calculated}}{C_{real}} \times 100\%$

Each measurement's error value has been calculated by using the formula above. The results are presented in Table 22 below.

Table 22. Measurements' errors.

C (mg/l)	Rhodes samples' error (%)	Helsinki samples' error (%)

0.15	0.88	3.59
0.5	-0.09	2.32
1	2.71	8.06
1.5	11.97	11.45
2	9.20	13.66
2.5	10.24	13.53

Ammonium standard's concentration is 1000 mg/l with a confidence interval ± 5 mg/l.

There were two samples; thus, to convert standard uncertainty, the confidence interval, which is 5 mg/l, has to be divided by 2 (95%). This results: $\frac{5}{2} = 2.5$.

To convert to relative uncertainty, standard uncertainty has to be divided by the concentration of the standard, which is 1000 mg/l, and this results:

$$u_{(cref)} = \frac{2{,}5}{1000} \times 100 = 0.25\ \%.$$

The next step is to calculate all results' bias by using the next formula.

$$bias = \frac{C_{calculated} - C_{real}}{C_{real}} \times 100\%$$

The results are presented in the table below.

Table 23. Bias.

C (mg/l)	Rhodes samples' bias (%)	Helsinki samples' bias (%)
0.15	5.87	23.92
0.5	-0.18	4.65
1	2.71	8.06
1.5	7.98	7.63
2	4.60	6.83
2.5	4.10	5.41

The bias standard deviation s_{bias}, calculation was made by using Microsoft Excel's standard deviation formula.

Rhodes: s_{bias}= 2.781

Helsinki: : s_{bias}= 7.223

When replacing all the values to the formula of u_{bias} the results are:

Rhodes: U_{bias}= 7.62 %

Helsinki: U_{bias}= 10.30 %

Table 24 presents a summary of all the statistical results of Rhodes and Helsinki samples' ammonium addition measurements.

Table 24. All the statistical results of Rhodes and Helsinki samples.

C (mg/l)	Standard deviation		Variance	t_{exp}	F_{exp}	error (%)		bias (%)	
	Rhodes samples	Helsinki samples				Rhodes	Helsinki	Rhodes	Helsinki
0.15	0.020	0.008	3.00036	2.848	6	0.88	3.59	5.87	23.92
0.5	0.039	0.02	3.00155	1.227	4	-0.09	2.32	-0.18	4.65
1	0.012	0.029	3.00077	3.843	5.42857	2.71	8.06	2.71	8.06
1.5	0.063	0.079	3.00816	0.115	1.53476	11.97	11.45	7.98	7.63
2	0.066	0.061	3.00647	1.111	1.17341	9.20	13.66	4.60	6.83
2.5	0.097	0.034	3.00843	0.717	8.24528	10.24	13.53	4.10	5.41

s_{bias}	
Rhodes samples	**Helsinki samples**
2.781	7.223
U_{bias}	
Rhodes samples	**Helsinki samples**
7.62 %	10.30 %

8 Discussion and Conclusions

By comparing Rhodes's and Helsinki's samples' pH average results, it can be concluded that there is not any difference between the two samples' pH value due to the fact that the pH value was stable in all measurements, at 7.7; thus, there is no difference between Helsinki's surface water's and Rhodes' groundwater's pH, at least in these specific cases.

Regarding the comparison between hardness results of the two samples, it can be concluded that groundwater, in this case Rhodes's water, contains more calcium and magnesium than surface water, Helsinki's water, which can be also noticed in cation measurements. Thus, Rhodes water samples' average hardness values are higher than those of Helsinki samples. This might happen due to the fact that groundwater moves through the soil and aquifers.

By comparing the average conductivity results of the two samples, it is concluded that Rhodes' samples have higher conductivity results which means that in Rhodes's water there are higher concentrations of inorganic dissolved solids, such as chloride, nitrate, sulfate, and phosphate anions or sodium, magnesium, calcium, iron, and aluminum cations, than in Helsinki's water.

By observing the results of anion and cation measurements, it can be noticed that both samples contain low concentrations of anions, and they do not exceed the maximum allowed limit, which EU's drinking water quality standards set. It is certain, however, that Rhodes's water contains higher concentrations of chlorine, which is caused possibly due to the fact that chlorine is added at the beginning of water's treatment and also at the end if needed. It is also certain that Helsinki's water contains higher concentrations of sulfate. In this case the reason might be that during the water treatment ferrous sulfate is added in order to purify water.

By measuring the concentrations of cations and by comparing the results of each sample, it can be concluded that Rhodes's water is richer in minerals than Helsinki's water. The reason is that Rhodes's water is groundwater as already mentioned, and groundwater moves slowly along the pores and fracture openings in rocks on the Earth's crust, where there is limestone, this influences water's chemical character. On the oth-

er hand, it is widely known that surface water has low concentration of minerals; thus, there are lower concentrations of these specific cations that were measured.

Neither sample contained carbonates. Rhodes's water contains higher concentration of bicarbonates; thus, it is more alkaline. It is known that in Finland daylight is limited in winter time, which means that photosynthesis does not occur at that time. This is the main reason why the bicarbonate concentration is lower in Helsinki's water because when there is daylight and thus strong photosynthetic activity, more bicarbonate ions are being produced in water.

Table 25. Ion balance.

Rhodes (meq/l)				Helsinki (meq/l)			
F-	0.005	Na^+	1.2	F-	0.005	Na^+	0.287
Cl^-	1.008	K^+	0.038	Cl^-	0.113	K^+	0.038
Br-	0.001	Ca^{2+}	1.058	Br	0	Ca^{2+}	0.083
SO_4^{2-}	0.128	Mg^{2+}	2.396	SO_4^{2-}	0.463	Mg^{2+}	1.625
NO_3^-	0.044			NO_3^-	0.019		
HCO_3^-	5.51			HCO_3^-	0.862		
Σ	6.696	Σ	4.692	Σ	1.462	Σ	2.033

Total dissolved solids measurements show also that in Rhodes's water, there are higher concentrations of inorganic and organic substances. The results were expected due to the fact that all the results of this study show that there is an agreement with the statement that groundwater contains more salts and minerals than surface water. [26, p.323]

By measuring the solutions of the water samples where specific amounts of ammonium standard solution were added, it can be concluded that the results of Helsinki's water values were on average higher than Rhodes's water values. By measuring the same solutions one day after the first measurement, it was observed that in Rhodes's water samples there was a more visible change in the results. The concentration of ammonium was reduced by an approximate 15% in Rhodes's water, while the corresponding value for Helsinki's water was approximately 5%. On the other hand, by measuring once more the same solutions seven days after the first measurement, it was observed that the concentration of ammonium was reduced even more, in Rhodes's water it was reduced by approximately 70% while the reduction in Helsinki's water was approxi-

mately 20%. This difference between ammonium reductions in the two countries' water samples may be explained due to the fact that in Rhodes's water there are more microorganisms, as a consequence of weather conditions, which are being fed on the ammonium concentrations being present in the water. Therefore, the metabolism of ammonium in Rhodes water's matrix is more excessive.

By measuring the ammonium content of the two countries' water samples, it was determined that Rhodes's water sample contained 0.03 mg/l NH_4, while Helsinki's sample contained 0.08 mg/l NH_4; thus, the ammonium concentration of Helsinki's water sample was higher than that of Rhodes's water sample. A statistical analysis of the samples by t-test, which examines if the correctness of the method is acceptable and also if the difference between the sample mean and the population mean is significant, showed that $t_{theor}>t_{exp}$, except for two values. Thus, the null hypothesis, which was established above in chapter 7, is rejected, and there is statistically significant difference in this method.

F-test compares two standard deviations. In this case, $F_{theor}>F_{exp}$, which means that null hypothesis, that standard deviations are equal, is accepted and the two standard deviations are equal and there is a 95% chance that any difference in the same standard deviations is due to random error.

The calculated errors and bias of each measurement showed that the average values of errors and bias in Helsinki's water sample were slightly higher than those calculated for Rhodes's water. This means that the values of the measurements of Helsinki's samples were not that close to the real value of ammonium's concentration as those of Rhodes's water, which might be caused due to the fact that Helsinki's water already contains a small but significant concentration of ammonium, which is higher than the concentration that exists in Rhodes's water. Also, regarding the results that are presented above in this chapter, it is concluded that Helsinki's water contains less microorganisms than Rhodes's water; this affects the way ammonium is being broken-down, which leads to the increment of ammonium's concentration due to the already existing concentration plus the concentration that has been added for the analysis. Considering these facts, it can be noticed that the two samples' matrices are reacting in a different way to the addition of ammonium.

By calculating u_{bias}, it was observed that its value for Rhodes's samples was lower than that for Helsinki's samples. This means that the two errors have not the same order of magnitude, and there is a statistically significant difference.

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Appendix 1. Definitions

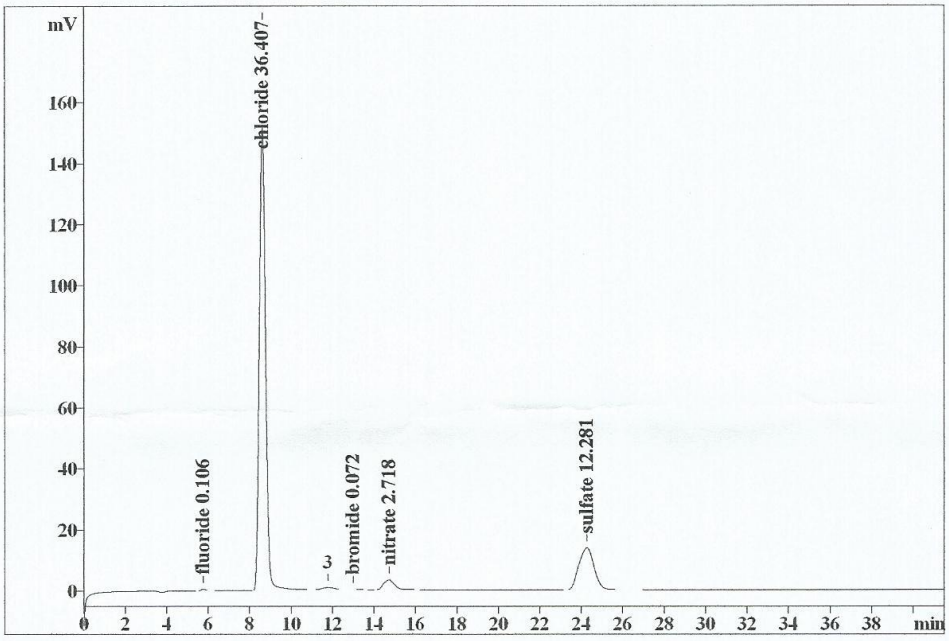
$C_{Calculated}$	The concentration that was resulted by measuring the samples.
C_{Real}	The concentration of the standard solutions.

Appendix 2. Rhodes' water analysis performed by Municipal Water Supply and Sewerage of Rhodes (DEYAR) [27]

Parameter	**Concentration in water supply's network of Deyar.**
pH	7,5-8,5
Conductivity	650-850
Turbidity	0,1-0,3
Nitrate	<5
Nitrite	<0,05
Ammonium	<0,1
Chloride	40-60
Sulfate	40-50
Total hardness	250-300 mgCaCO3/l
Fluoride	0,12-0,14
Total organic carbon	0,4-0,7 mg/l
Aluminum	<20
Arsenic	<1
Antimony	<0,5
Benzo-a-pyrene	0
Benzene	0
Vinyl Chloride	0
Bromates	<0,3
Epichlorohydrin	0
Cadmium	<0,5
Manganese	0-13
Magnesium	45-55 μg/l
Lead	0-3 μg/l
Sodium	40-50
Nickel	<5
Iron	0-60
Copper	0-0,07
Chromium	5-16
Zinc	15-20 μg/l
Mercury	<0,2
Total Biocides	0
Total coliforms	0
E. coli	0
Enterococcus	0
Total bacteria 37^{o} C	0-15
Total bacteria 22^{o} C	0-15

Appendix 3. Anions' (F^-, Cl^-, Br^- , NO_3^-, SO_4^{2-}) chromatogram of Rhodes' samples

SAMPLE: 1
: 1
Vial number: 3
Volume: 1.0 µL
Dilution: 1.00
Amount: 1.0000



Quantitation method: Custom

No	Retention min	Height mV	Area mV*sec	Resolution n,n+1	TP	Conc. mg/L	Name
1	5.75	0.57	10.984	5.56	2019	0.106	fluoride
2	8.62	151.53	3165.828	3.85	3855	36.407	chloride
3	11.78	0.72	28.649	1.29	2001	0.000	System Peak
4	12.99	0.10	2.900	1.92	4679	0.072	bromide
5	14.72	3.22	117.270	7.96	3696	2.718	nitrate
6	24.27	13.81	704.364	0.00	5122	12.281	sulfate
6	41.52	169.94	4029.995		3562	51.583	

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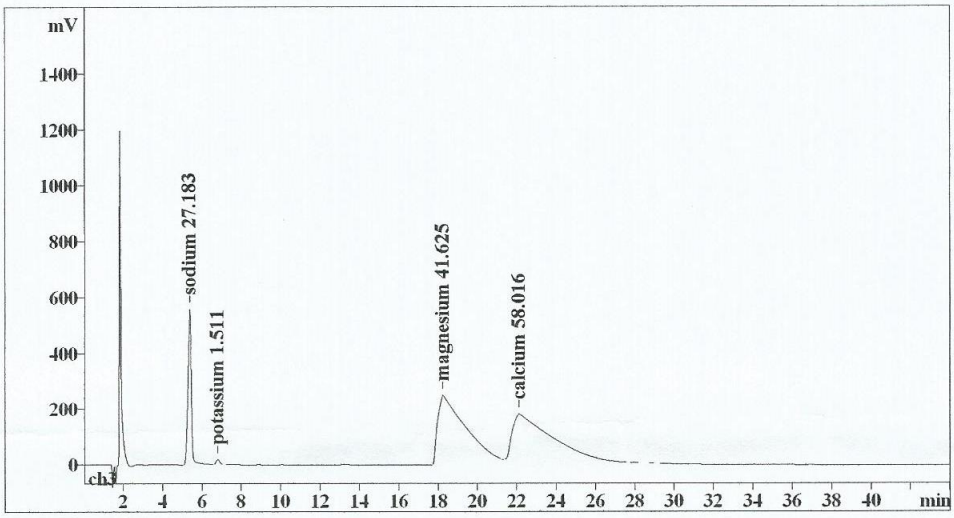
Appendix 4. Cations' (Na^+, K^+, Ca^{2+}, Mg^{2+}) chromatogram of Rhodes' samples

SAMPLE:
:
Vial number: 2
Volume: 1.0 µL
Dilution: 1.00
Amount: 1.0000



Quantitation method: Custom

No	Retention min	Area mV*sec	Resolution n,n+1	TP	Conc. mg/L	Name
1	5.39	6355.061	4.59	5077	27.183	sodium
2	6.79	203.083	8.44	7051	1.511	potassium
3	18.25	22996.448	1.35	863	41.625	magnesium
4	22.13	22840.937	0.00	579	58.016	calcium
4	44.00	52395.528		3392	128.335	

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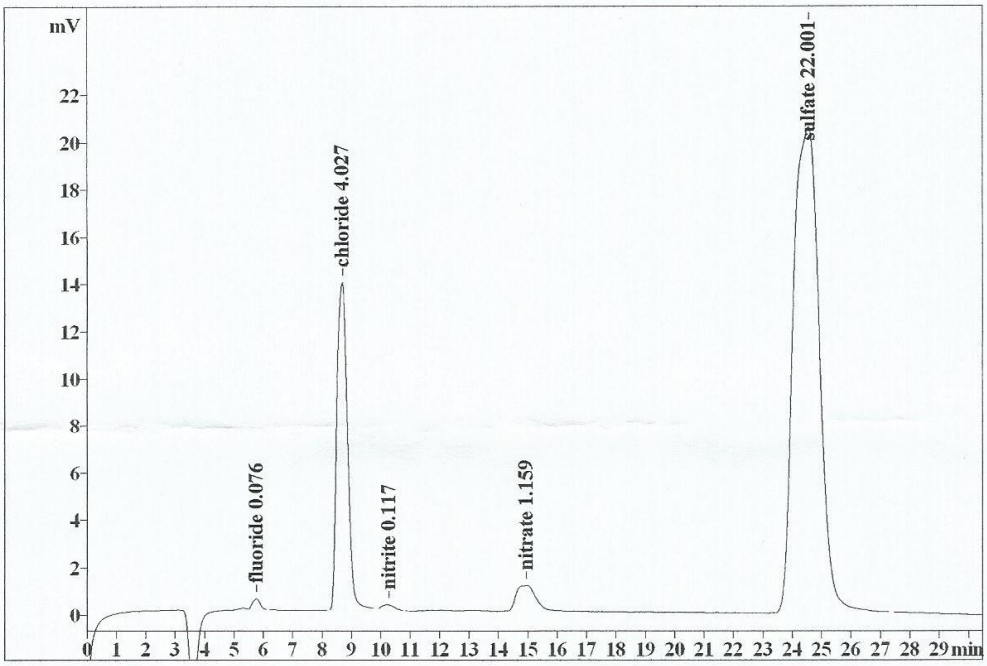
Appendix 5. Anions' (F^-, Cl^-, Br^- , NO_3^-, SO_4^{2-}) chromatogram of Helsinki's samples

SAMPLE: 1
: 1
Vial number: 13
Volume: 1.0 µL
Dilution: 1.00
Amount: 1.0000



Quantitation method: Custom

No	Retention min	Height mV	Area mV*sec	Resolution n,n+1	TP	Conc. mg/L	Name
1	5.77	0.45	7.870	4.85	2415	0.076	fluoride
2	8.68	13.86	350.186	2.02	2671	4.027	chloride
3	10.27	0.20	6.045	4.34	2788	0.117	nitrite
4	14.96	1.09	50.028	6.25	2433	1.159	nitrate
5	24.55	20.55	1261.849	0.00	3616	22.001	sulfate
5	30.49	36.15	1675.978		2784	27.380	

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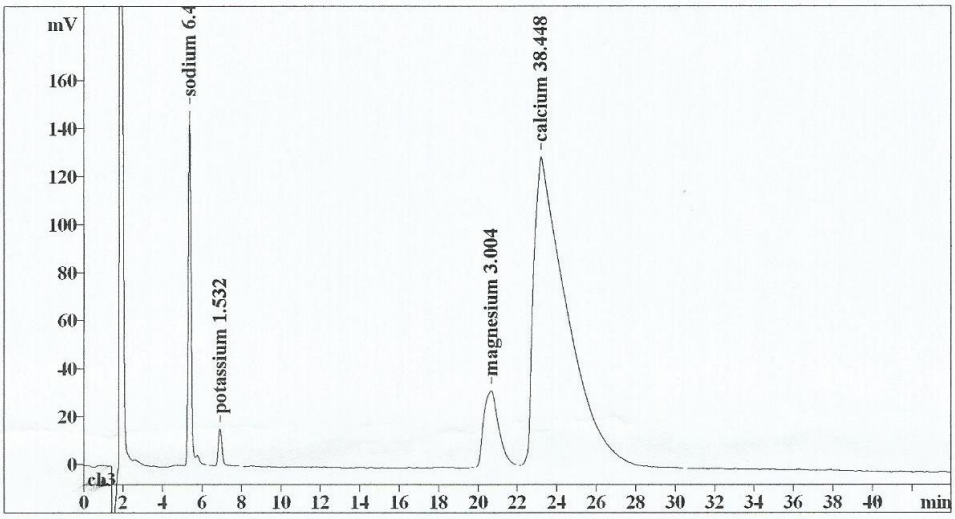
Appendix 6. Cations' (Na^+, K^+, Ca^{2+}, Mg^{2+}) chromatogram of Helsinki's samples

SAMPLE:
:
Vial number: 4
Volume: 1.0 µL
Dilution: 1.00
Amount: 1.0000



Quantitation method: Custom

No	Retention min	Area mV*sec	Resolution n,n+1	TP	Conc. mg/L	Name
1	5.37	1504.690	5.16	6313	6.436	sodium
2	6.91	205.905	15.57	6159	1.532	potassium
3	20.68	1659.818	1.18	3565	3.004	magnesium
4	23.21	15137.069	0.00	881	38.448	calcium
4	44.00	18507.483		4230	49.420	

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